



Pt-modified molybdenum carbide for the hydrogen evolution reaction: From model surfaces to powder electrocatalysts

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H I G H L I G H T S

- We investigate Mo₂C catalysts modified by Pt for the hydrogen evolution reaction.
- Thin films of Mo₂C supporting a Pt monolayer displayed activity similar to bulk Pt.
- Results from thin film surfaces were scaled to powder electrocatalysts.
- Pt-modified Mo₂C powders showed high activity and stability.

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This work explores the opportunity to substantially reduce the cost of hydrogen evolution reaction (HER) electrocatalysts by supporting one monolayer (ML) of platinum (Pt) on low-cost molybdenum carbide (Mo₂C) substrate. These efforts were primarily directed towards scaling a thin-film catalyst to high surface area particles. Electrochemical experiments investigated single-phase Mo₂C thin films modified by different coverages of Pt for the HER. The ML Pt–Mo₂C thin film showed Pt-like HER activity while displaying excellent stability under HER conditions. The promising results on thin films were then extended to more practical powder catalysts. Samples of various Pt loadings on Mo₂C powders were synthesized using the co-impregnation method and were evaluated for HER activity. The ability to successfully link electrochemical activity on thin films and powder catalysts was thus demonstrated.

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1. Introduction

Low-temperature water electrolyzers show promise as sources of hydrogen. For example, a proton exchange membrane (PEM) electrolyzer can produce H₂ at high levels of pressure and purity. As compared to traditional alkaline electrolyzers, a PEM cell does not contain a caustic liquid electrolyte that is difficult to transport. However, due to the acidic environment and need for high current density, PEMs utilize scarce and expensive precious metals such as platinum (Pt). With the demand for hydrogen and the extensive development of fuel cells and PEM electrolyzers, the global reserves of Pt are gradually decreasing. Therefore, it is necessary to search for alternative electrocatalysts that substantially decrease or eliminate altogether the amount of Pt, without losing the performance of conventional Pt electrocatalysts.

One method of minimizing Pt loading is to use metal carbides as support materials for one monolayer (ML) of Pt. Recent findings have shown that Pt monolayer supported on tungsten carbide (Pt/WC or W₂C) showed HER activity almost identical to that of Pt bulk foil [1]. However, the synthesis of WC requires extremely high temperatures that could promote the sintering of small WC particles into larger ones, decreasing the surface area [2]. Another metal carbide, molybdenum carbide (Mo₂C), can be synthesized at lower temperatures and thus has a higher surface area than WC. Recently, porous Mo₂C catalysts were synthesized with a surface area of 94 m² g^{−1} and were active for the hydrodeoxygenation of C3 oxygenates to alkenes [3]. Additionally, Mo₂C has shown to be a promising support material in both gas-phase and electrochemical systems [4,5]. Moreover, similar to WC, Mo₂C is electrochemically stable at HER conditions in acidic solution [6,7]. Pt-modified Mo₂C has previously been used as a catalyst for cellulose conversion to polyols [8] and the water-gas shift reaction [9]. Additionally, Pt/Mo₂C was studied as an electrocatalyst for the oxygen reduction

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reaction [10]. This prior work makes Mo₂C a promising material to support ML Pt as low-cost HER electrocatalysts.

There are two primary objectives in the current study. First, we seek to explore Pt-modified Mo₂C HER catalysts by studying the deposition of sub-ML to ML amounts of Pt loadings on single-phase Mo₂C thin films. Previously, HER activity was shown to be correlated to the hydrogen binding energy (HBE) in both monometallic and bimetallic alloys [11,12]. Materials such as the Pt-group metals have intermediate HBE values, which result in high HER activity. In the current study, electrochemical experiments were conducted to evaluate the activity and stability of single-phase Mo₂C and ML Pt/Mo₂C films. Polycrystalline Mo₂C foils were synthesized using temperature programmed reaction with methane and hydrogen. Multiple coverages of Pt were deposited on the foils by physical vapor deposition (PVD). X-ray photoelectron spectroscopy (XPS) was used to verify the carbide stoichiometry and overlayer coverage of Pt. Electrochemical measurements such as linear sweep voltammetry (LSV) and chronopotentiometry (CP) were utilized to assess the activity and stability of the Pt/Mo₂C electrocatalysts. Finally, XPS characterization was compared before and after electrochemical experiments to determine catalyst stability.

The second objective of this study is to scale up the ML Pt–Mo₂C thin film system to more commercially viable powder electrocatalysts. The motivation for synthesizing catalysts in powder form is driven by their high surface area and ease of impregnation on carbon paper. HER measurements were conducted to compare samples of Mo₂C with different loadings of Pt with 10 wt% Pt supported on high surface area carbon (Pt/C) to determine whether Pt–Mo₂C powder showed good catalytic activity for HER in acidic environment as predicted from the results on ML Pt–Mo₂C thin films.

2. Methods

2.1. Synthesis and characterization of Pt-modified Mo₂C thin films

Polycrystalline Mo foils (Alfa Aesar, 99.95%, 0.1 mm) were rinsed with deionized (DI) water and methanol, and dipped in a 0.3 M NaOH solution for one minute (Fisher Scientific, 99.5%), which has been shown to remove surface oxides [7,13]. The treated foils were placed within a Lindberg furnace (model 55035) to synthesize Mo₂C by direct carburization with methane (CH₄) and hydrogen (H₂) using flow rates of 33 and 122 sccm (molar ratio 21% and 79%), respectively. The high temperature synthesis step for Mo₂C was carried out at 850 °C. At the end of the synthesis procedure, H₂ was fed for two hours to remove excess surface carbon, as previously verified using XPS [14]. The samples were then exposed to a mixture of 1% O₂ in 99% N₂ for three hours at room temperature to passivate the surface defects to prevent severe oxidation upon exposing Mo₂C to atmospheric oxygen.

The Mo₂C foils were rinsed with DI water, methanol, and dipped in a 0.3 M NaOH solution for one minute. Within ten minutes of ambient exposure, the samples were transferred into a PVD chamber with a base pressure of 1×10^{-8} Torr. A 0.5 mm diameter tungsten filament with a 0.2 mm diameter Pt wire (Alfa Aesar, 99.9%) coiled around the filament was resistively heated to evaporate Pt on the Mo₂C substrate. This thermal evaporation method has been commonly employed in the preparation of ML metal over carbide surfaces [15].

Once the Pt/Mo₂C samples were synthesized, they were transferred into a Phi 5600 XPS chamber within ten minutes of ambient exposure. The XPS was calibrated using the reported binding energies of Au, Ag, and Cu reference thin films [16]. The Pt overlayer coverage was calculated using the inelastic mean free path (IMFP) values provided in Cumpson and Seah [17]. Further details can be

found in previous publications [1,18]. After the electrochemical experiments, the samples were transferred into the XPS chamber within ten minutes of ambient exposure for further characterization.

2.2. Preparation and characterization of Pt/Mo₂C powders

For each experiment, 20 μ L of ink sample was dropped onto the center of a glassy carbon substrate. The ink was an aqueous suspension of ~ 2.6 mg of catalyst/mL of solvent produced by ultrasonically dispersing a metal loading of 0.0025, 0.005, 0.01, 0.02, 0.04, 0.06, 0.08, 0.1 (g of catalyst/g of support) for 1 h in deionized water. The catalyst was prepared by co-impregnating Pt metals on Mo₂C immersed in an oil bath at a temperature of ~ 65 °C until all of the water was evaporated, followed by a 2 h calcination process at 290 °C in order to remove volatile fractions such as NO₃[−] from the respective precursors. Once the metal was uniformly dispersed in water solvent, the ink was dropped onto the glassy carbon electrode by forming a ring of droplets on the outside edge of the disk, and then filling the middle with the remainder of the ink. This procedure was calculated to yield a catalyst loading of 10 μ g cm^{−2} for a standard electrode geometric surface area of 0.196 cm². After the ink dried on the electrode, a single drop of Nafion was pipetted onto the catalyst and allowed to dry for a stronger binding between the catalyst and the surface of the electrode. Inductively coupled plasma (ICP) was used to test for dissolution of Pt/Mo₂C powders from the disk into the electrolyte solution.

2.3. Electrochemical measurements

Electrochemical measurements were performed using a three-electrode glass cell containing 0.5 M sulfuric acid solution (H₂SO₄, Fisher Scientific, 96.9%) using a Princeton Applied Research Versastat 4 potentiostat. The solution was prepared with DI water purified to a resistivity above 17 M Ω -cm by a Barnstead NAN-Opure filtration system. Pt gauze (Alfa Aesar, 99.9%) was used as the counter electrode. Twenty-five cyclic voltammetry (CV) scans between 0 and 0.4 V vs NHE were used to clean and condition the Pt/Mo₂C electrode surfaces, and scans in the range of 0–1.4 V were used to clean the Pt reference wire. LSV measurements from +0.1 to −0.4 V vs NHE at a sweep rate of 2 mV s^{−1} were used to measure the HER activity by generating Tafel plots. LSV measurements were performed in Ar-purged solution with a saturated calomel electrode (SCE) used as the reference. Chronopotentiometry (CP) was used to measure the electrochemical stability of the samples over two hours of HER operation; alternating periods without current for five minutes and 10.0 mA cm^{−2} for twenty-five minutes were used to simulate the intermittent operation typical of an electrolysis device. A Pt wire with H₂ bubbled through the solution to maintain saturation was used as an internal reference electrode for the CP experiments.

3. Results and discussion

3.1. Structure and activity of thin films

The Pt/Mo₂C thin film system was first evaluated to determine its growth mechanism by using XPS. Fig. 1 shows the Pt coverage as a function of deposition time on a thin Mo₂C film. The increase in Pt film thickness was linear with respect to deposition time, suggesting that Pt growth was layer-by-layer on Mo₂C. The layer-by-layer mechanism agrees with that seen previously for Pt on a WC substrate [1].

The Pt-modified Mo₂C thin films, with different Pt coverages, were evaluated for HER activity. Fig. 2 shows a CV performed in Ar-

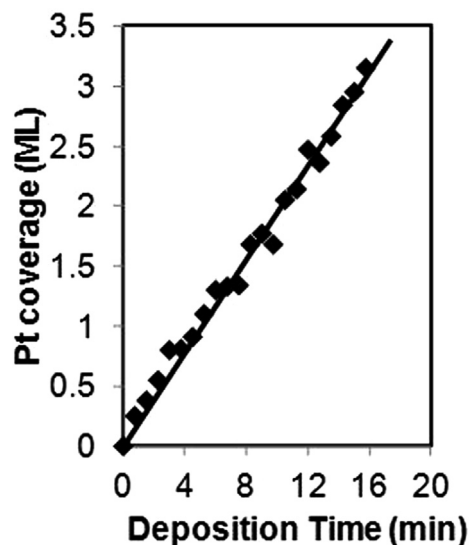


Fig. 1. Pt coverage as a function of deposition time on Mo₂C, as measured by XPS.

saturated 0.5 M H₂SO₄ on 1.45 ML Pt/Mo₂C. At this Pt coverage, no peaks due to hydrogen adsorption and desorption are visible. Additionally, the surface begins to oxidize at 600 mV vs NHE. For this reason, we only performed cleaning scans to 400 mV. Fig. 3 shows the LSV measurements performed on Mo₂C, Pt, and Pt-modified Mo₂C. As expected, the current density shown on unmodified Mo₂C was extremely low, but modification with 0.5 ML Pt produced a substantial increase in current density. Tafel plots generated from the LSV data also show a substantial difference between Mo₂C and Pt-modified Mo₂C. As shown in Fig. 4, the activity of Pt overlayers above 0.5 ML was indistinguishable from Pt foil at low current densities. The reversible potential for hydrogen evolution was calculated by using the Nernst equation with pH calculated from the acid concentration. Also, the overpotential was corrected by performing a CV of Pt foil from 0 to 1.4 V vs NHE. The peak locations for hydrogen desorption in the CV were shifted by -0.05 V with respect to the literature values on polycrystalline Pt [19]. Adding the Nernst value to this correction resulted in the reversible potential of -0.068 V with respect to the measured overpotential, as indicated on Fig. 4. The current on each surface at this potential was extracted and plotted versus Pt coverage in Fig. 5. For bare Mo₂C, the log of the exchange current density was -6.1 , about three orders of magnitude lower than Pt foil. Modification of Mo₂C with even 0.5 ML Pt resulted in substantial enhancement of

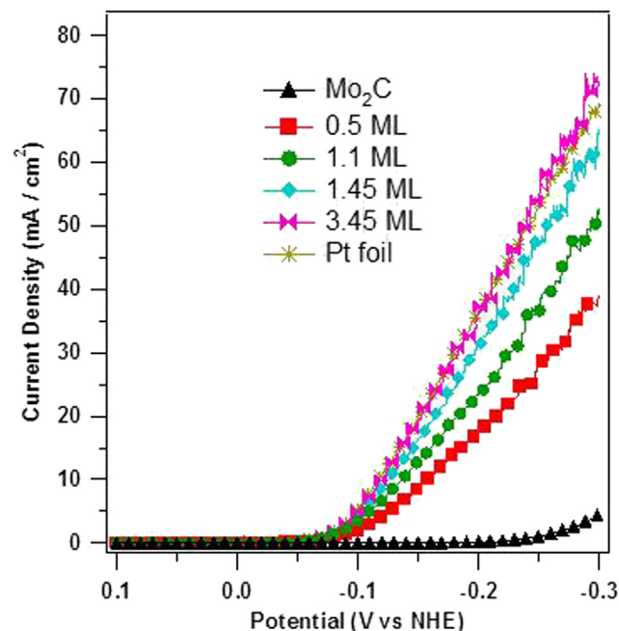


Fig. 3. Linear sweep voltammograms of Mo₂C and Pt-modified Mo₂C in Ar-saturated 0.5 M H₂SO₄, recorded at a sweep rate of 2 mV s⁻¹. Pt foil is provided for comparison.

HER activity. The activity observed for the HER on the Pt/Mo₂C system agrees with that observed previously for Pt/WC, where a monolayer of Pt effectively behaved like bulk Pt [1].

Long-term stability tests also demonstrated the effectiveness of Pt-modified Mo₂C as HER catalysts. During the experiment, two different segments were studied: first, a 5-min period with no current, then a 25-min period with a reducing current of 10 mA cm⁻². The sequence was repeated over a two hour period. The results from a 2-h chronopotentiometry experiment in H₂-saturated 0.5 M H₂SO₄ are shown in Fig. 6. For bulk Mo₂C, the open-circuit potential was about +500 mV vs NHE, indicating surface oxidation and corrosion. During hydrogen evolution, the overpotential on Mo₂C was between 300 and 350 mV. Upon Pt modification, the open-circuit potential was close to the NHE. Additionally, the operating overpotential drastically decreased. At a coverage of 1.5 ML, the operating overpotential was about 70 mV,

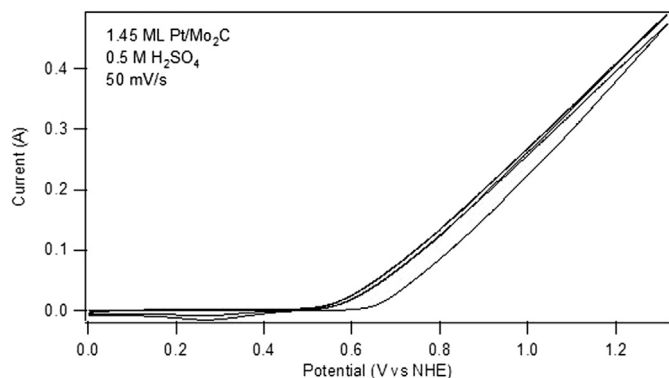


Fig. 2. Cyclic voltammogram of 1.45 ML Pt/Mo₂C, performed in Ar-saturated 0.5 M H₂SO₄ at a sweep rate of 50 mV s⁻¹.

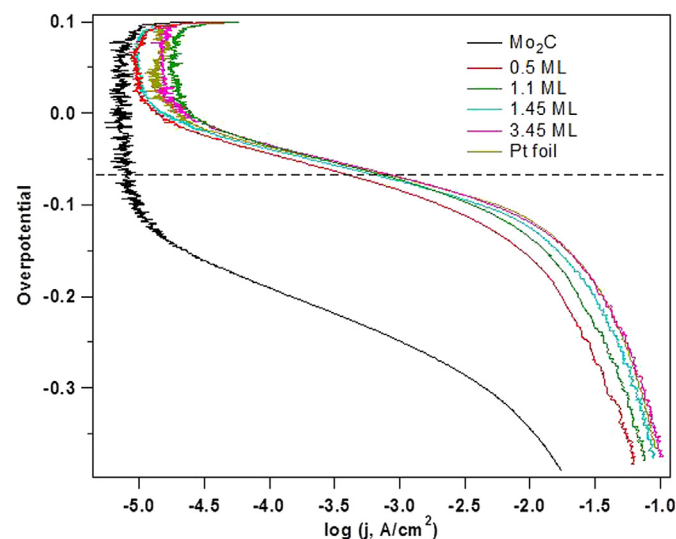


Fig. 4. Tafel plots for Mo₂C and Pt-modified Mo₂C from LSV data. The reversible potential for hydrogen evolution is indicated by the dashed line.

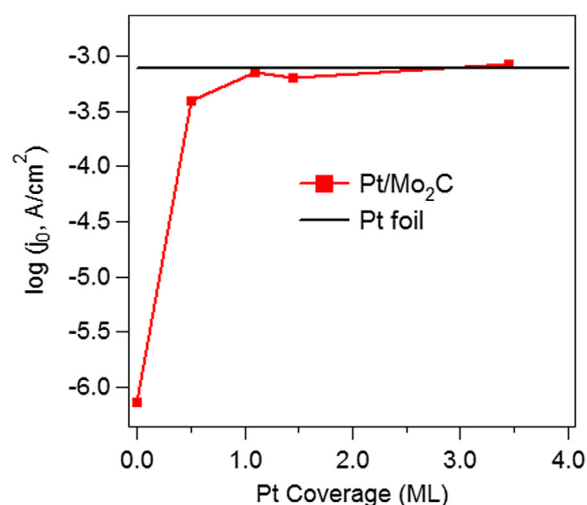


Fig. 5. Logarithm of the exchange current density for hydrogen evolution on Pt/Mo₂C foils.

about the same as that of Pt foil (data not shown). The overpotential did not increase over time for this sample, indicating the stability of the Pt overlayer on Mo₂C.

Finally, XPS characterization of Pt-modified Mo₂C thin films demonstrated its electrochemical stability. Fig. 7(a) shows the XPS spectra for 1.5 ML Pt/Mo₂C, before and after electrochemical experiments. As expected from the stable chronopotentiometry results, the Pt 4f signal did not decrease noticeably with respect to the Mo 3d signal after experiments. This is reflected in Fig. 7(b), which shows the Pt 4f/Mo 3d ratio for 1.1 and 1.5 ML Pt/Mo₂C thin films. For the lower-coverage sample, the intensity ratio did decrease slightly. This may be due to Pt aggregation or dissolution, or dissolution of MoO_x species formed during the cleaning CV. The 1.5 ML sample actually showed a slight increase in the Pt 4f/Mo 3d ratio. The experimental results indicate little Pt aggregation or dissolution.

3.2. Extension to powder catalysts

Despite the promising results on thin films, further research is needed before metal-modified carbides can be considered viable

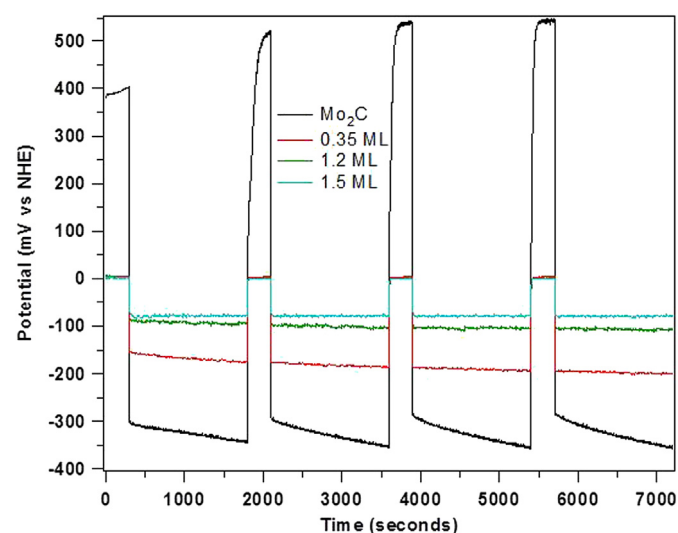


Fig. 6. Chronopotentiometry measurements on Mo₂C and Pt-modified Mo₂C in H₂-saturated 0.5 M H₂SO₄. Current alternated between no current and -10 mA cm^{-2} .

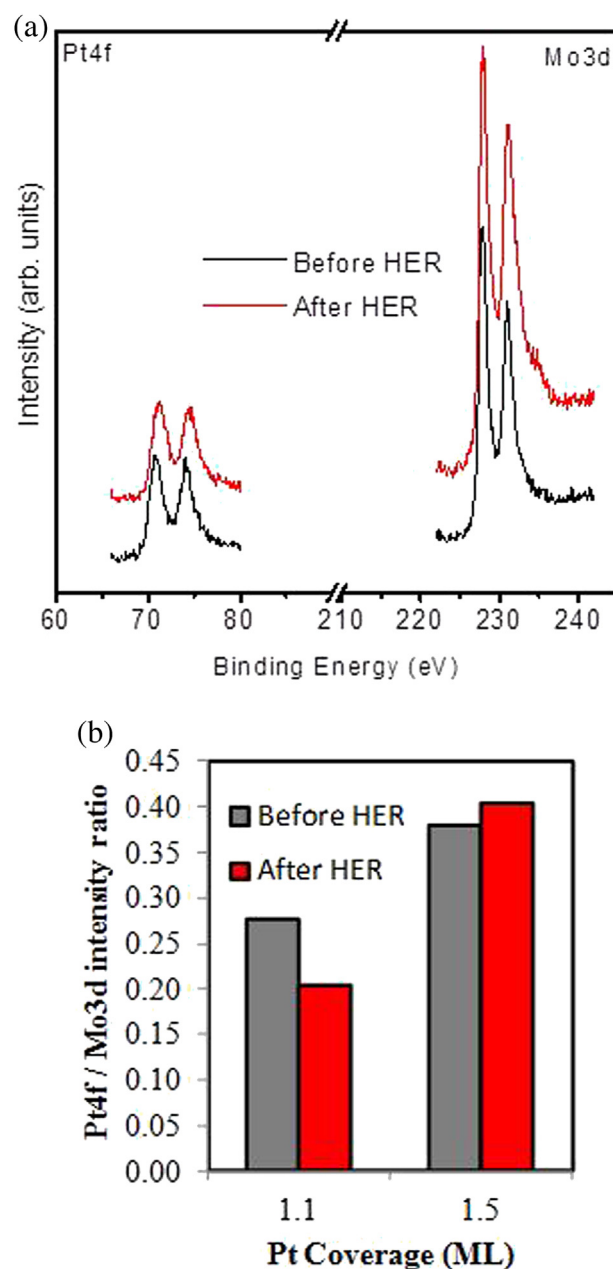


Fig. 7. (a) XPS spectra of Mo3d and Pt4f regions on 1.5 ML Pt/Mo₂C before and after electrochemistry and (b) Pt4f/Mo3d intensity ratio before and after electrochemistry for Pt/Mo₂C samples.

HER electrocatalysts. Powder catalysts with various loadings of Pt on Mo₂C were synthesized and tested for HER activity. The similarity of Pt/Mo₂C powders to Pt/C can be seen in the CV plots of Fig. 8. Unmodified Mo₂C shows very broad, undefined peaks for the adsorption and desorption of H⁺. Upon modifying the Mo₂C powders with 0.25 wt % Pt, a distinct peak at 190 mV vs NHE can be observed. At higher loadings of 2 wt % and above, these peaks are well-defined similar to the Pt/C standard. LSV measurements also showed a similar trend. The log of the exchange current densities were calculated from the Tafel parameters and are plotted against Pt wt% loadings on Mo₂C, as shown in Fig. 9. The exchange current density of the 10 wt% Pt/C catalyst is represented by the straight line. For unmodified Mo₂C powders, the log of the exchange current density was -4.31 , about two orders of magnitude lower than Pt/C.

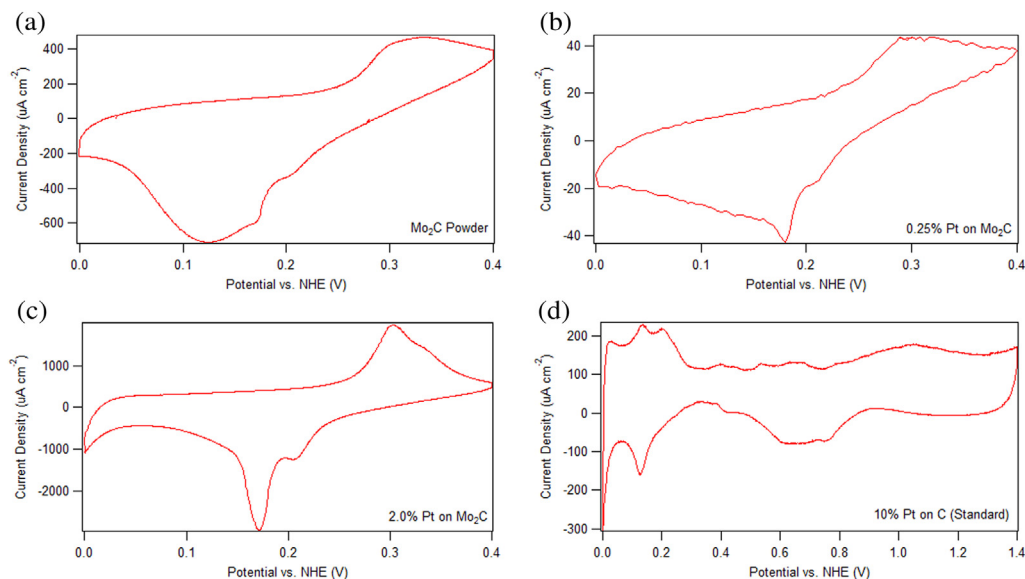


Fig. 8. Cyclic voltammetry measurements on (a) Mo₂C powders, (b,c) Pt-modified Mo₂C, and (d) 10 wt% Pt/C.

Increasing the Pt wt% resulted in the Pt/Mo₂C current density being close to the Pt/C value, in agreement with the results on thin films. As little as 0.25 wt% Pt on Mo₂C was capable of increasing the HER activity significantly from unmodified Mo₂C. At 2 wt% of Pt the HER activity became comparable to that of the Pt/C catalyst.

Because catalysts in powder form, with the addition of Nafion, prevent the use of XPS after electrochemical experiments, an inductively coupled plasma (ICP) with Mo and Pt ICP standards in nitric acid was used to determine the possible dissolution of the Pt/Mo₂C catalyst. Measurements from ICP are shown in Table 1. Results indicated that electrolyte solutions for Pt/Mo₂C samples show the presence of Mo in the range of 30–40 ppb. Furthermore, ICP measurements showed only trace amounts of Pt. This analysis altogether suggests that while there was a small amount of catalyst present in the solution, dissolution of the sample was insignificant.

4. Conclusions

The modification of Pt on Mo₂C for hydrogen evolution catalysts was explored to better understand the scaling from thin film model surfaces to higher surface area particles. First, Pt/Mo₂C thin films were found to be electrochemically active for hydrogen evolution and stable after two hours of HER. In this regard, the results for Pt on Mo₂C agreed with earlier experiments for Pt on WC.

Table 1

Inductively-coupled plasma measurements of electrolyte solution following electrochemical experiments with Pt/Mo₂C powders. Concentration given in parts-per-billion. Numbers following element names indicate detection wavelength, and RSD represents relative standard deviation of the samples.

Sample	Mo 202.030	Mo 281.615	Pt 214.425	Pt 265.945
1	50	40	10	10
2	40	30	10	10
3	40	30	0	10
4	40	30	10	10
RSD (%)	17.54	14.47	10.95	17.29

Then, Pt/Mo₂C core–shell particles were synthesized using a co-impregnation method to deposit various Pt wt% on Mo₂C powder substrates to compare the ML Pt/Mo₂C thin film system to more commercially viable electrocatalysts. In terms of reducing the Pt loading while maintaining Pt bulk-like performance, the Pt/Mo₂C core–shell powder catalysts produced HER results that are quite similar to that of the ML Pt/Mo₂C thin films. Both thin film and powder catalysts showed substantial enhancement in HER activity when Pt was deposited onto Mo₂C substrates. These combined results demonstrate the ability to use a model structure for verification, and then synthesize a practically useful electrocatalyst. Further work should involve optimization of synthetic methods to better develop a new class of electrocatalysts.

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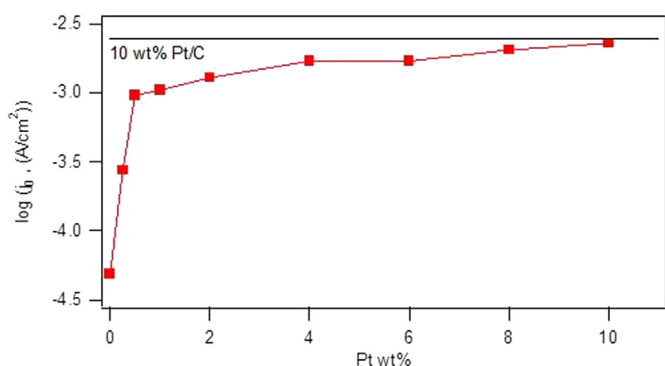


Fig. 9. Logarithm of the exchange current density for hydrogen evolution on Pt/Mo₂C powders.

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